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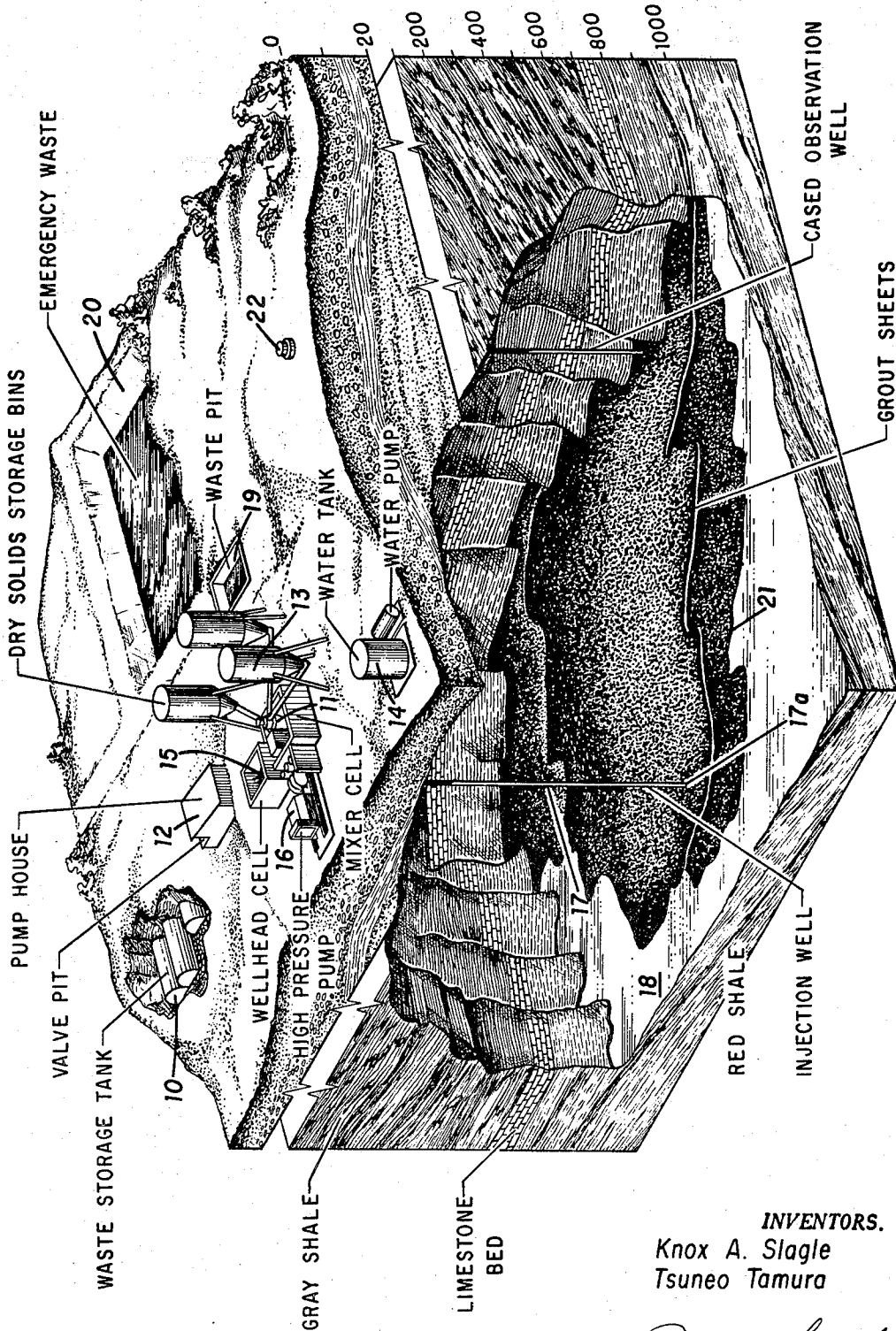
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METHOD OF DISPOSING OF WASTE MATERIALS

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SCALE IN FEET



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METHOD OF DISPOSING OF WASTE MATERIALS

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ABSTRACT OF THE DISCLOSURE

A method of disposing of radioactive waste materials, wherein the materials are added to a hydraulic cement slurry comprising attapulgite and illite type clays, the cement slurry is pumped into an earth formation under fracturing pressure and allowed to set in the fractures created.

The present invention relates to a new and improved method of disposing of waste materials by hydraulic fracturing and particularly to a method of disposing of radioactive wastes or materials.

U.S. Patent No. 3,108,439 discloses a number of prior art methods of disposing of radioactive waste materials and particularly a method of underground disposal of radioactive liquids or slurries wherein an impermeable rock formation is fractured and the radioactive slurry injected thereinto and subsequently injecting a sealing material into the impermeable formation to thereby seal the radioactive slurry in the impermeable rock formation.

The process of said prior art patent is carried out by first drilling a well so that it traverses a suitable formation with the depth selected to give adequate shielding from the most energetic fraction to be handled. The well is then equipped with a casing which is sealed both above and below the fracturable formation, for example, with cement to insure its isolation. In the simplest case, the formation is fractured in a substantially horizontal direction. This may be performed according to any of the several recognized techniques, namely, gun perforating, pre-slotting the pipe, acid cutting, and the like, followed by injection of any suitable fracturing fluid. If desired, the formation can be fractured by using radioactive waste liquid or slurry as the fracturing fluid. The waste can be employed alone or in combination with any of the conventional fracturing fluids or fracturing fluid additives, for example, fluid loss additives.

An important factor in carrying out the prior art invention is to open a single fracture in a substantially horizontal direction. It will, of course, be well understood by those skilled in the art that fractures of the nature contemplated by this prior art invention will not always run out from the wellbore in an exact, or even substantially, horizontal direction; but in any event such fractures will be at an angle with respect to the axis of the wellbore. When a conventional fracturing fluid is used, ordinarily this fluid is removed from the system and radioactive waste substituted therefor in the fracture. If desired, the fracture can be propagated by injecting radioactive waste fluid at a pressure greater than the formation breakdown pressure. When deemed appropriate, fracturing is sealed to prevent escape of the radioactive waste.

While a simple case involves only a single fracture, it is possible and in general, will be found desirable to isolate this fracture and initiate others from the same well. In such case, then, it is possible to deposit waste in a plurality of fractures radially disposed from a single well. Heat is continuously given off by the radioactive waste and must be eventually removed from the formation. In

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view of this, it is necessary to hold the number of said radiating fractures at some minimum and thereby limit the total quantity of radioactive waste to an amount which will allow dissipation of heat from the formation. The amount of radioactive waste which can be stored is dependent on the level of the radioactivity of the particular waste, the size of the formation in which the waste is disposed, and the location of the fractures within the formation. The amount of heat evolved can readily be determined by calculations from the level of radioactivity of the waste. The foregoing measures are taken to insure adequate heat dissipation and thereby prevent excessive temperatures and pressures within the formation.

A somewhat more detailed description of the prior art method is as follows:

A well is drilled so as to traverse an impermeable, non-foraminous formation. The formation is isolated as by cementing. The nonporous formation is perforated by, for example, gun perforation. It may be found desirable to isolate the perforated zone with packers in some cases. The fracturing fluid which may be the radioactive waste is pumped into the well under pressure, thereby building up a hydrostatic pressure. When the hydrostatic pressure exceeds the formation breakdown pressure, the formation will part or fracture. The pressure ceases to rise as fluid is injected and assumes a roughly constant value. The fluid pressure measurements at the surface indicate that the formation breakdown pressure has been reached. Inasmuch as the pressure required to overcome the rock bounding strength is small at great depth in comparison to the pressure required to lift the effective overburden, the pressure drop may be small when the formation breakdown pressure is reached. The formation breakdown pressure, therefore, may be more accurately defined as the pressure at which the increase of the rate of fluid injection into the formation will not materially increase the fluid pressure. When deemed proper, depending upon particular existing conditions, waste injection is stopped; and the fracture is sealed, as for example, by cementing. The same procedure then may be repeated at a different level of the same formation.

The present invention utilizes the formation fracturing procedures hereinabove and is an improvement of this prior art method of waste disposal by fracture injection wherein cement and other additives are mixed or blended with the waste slurry to form a low viscosity pumpable slurry which sets into a hard mass after a predetermined time.

It is a primary object of the present invention to provide a practical and economic method of disposing of waste materials, particularly radioactive waste materials by hydraulic fracturing.

It is a particular object of the present invention to provide a waste material cement-containing slurry which has a low viscosity, is pumpable for relatively long periods of time, will set with at least moderate strength and will not be subject to phase separation.

It is an important object of the present invention to provide a waste material cement-containing slurry which will retain radioactive nuclides.

Other objects and advantages of the present invention will become readily apparent from a consideration of the following description and drawing, wherein:

The drawing illustrates a schematic perspective view of a typical fracturing disposal plant for carrying out the method of the present invention and a partially sectional view of the earth formation beneath the plant.

In the drawing, radioactive waste fluids or materials are stored in suitable storage tanks 10. Underground lines connect the storage tanks to a source of supply (not shown) and to the mixing equipment 11. A pump

house 12 has pumps located therein and suitably connected to the underground lines for pumping the waste material to the mixing equipment in the mixer cell.

Several dry solids storage bins 13 are conveniently located around the mixer cell for introducing cement, clays and other additives into the waste fluid for blending therewith. The mixer cell contains suitable blending and mixing equipment 11, such as a dry solid blender and a jet mixer.

A water supply source 14 is also located nearby for providing water when the liquid content of the waste is less than that desired for preparing a suitable injection slurry or for such other uses as may be desired, and is connected to the mixing equipment or apparatus 11 by an underground line.

Additional underground lines connect the mixing equipment 11 to the wellhead fracturing manifold or Christmas tree 15.

A high pressure fracturing pump 16 is installed adjacent the mixer cell for pumping the slurry of the present invention from the mixing equipment 11 into the wellhead 15 and down the cased wellbore 17 into the earth formation 18.

A waste pit 19 is located near the mixer cell to catch any overflow or leakage from the wellhead 15 or the mixing apparatus 11. Suitable drainage is provided for enabling any excess or overflow slurry to run into the waste pit 19. The waste pit is connected to both the mixing apparatus 11 and the storage tank 10 by underground lines so that fluids collected therein may be disposed of when convenient.

Also, an emergency trench or pit 20 is located near the waste pit 19 for collecting any overflow fluids therefrom. Sufficient drainage is provided for this.

Suitable shielding such as concrete, earth or other materials for protection from radioactive materials is placed around the various plant components.

The injection well 17 is cased from the wellhead 15 to its lower end 17a to prevent fluids from escaping into areas of the formation in which no slurry is injected.

The drawing of the earth formation is partially cut-away so that the distribution of the slurry 21 into the earth formation 18 may be readily seen.

One or more cased observation wells 22 are located on the perimeter of the plant site for viewing the distribution of the slurry 21 in the earth formation 18.

It can be appreciated that the drawing is illustrative of only one type of installation which can be used in carrying out the method of the present invention. Any equipment and arrangement thereof for blending a cement-waste slurry and for fracturing an earth formation therewith may be used without departing from the scope of the present invention.

In hydraulic fracturing of underground earth formations, there is a perceptible movement of the formation above the fracture injection. This movement of the overburden formation frequently causes shifts in the underground stratas so that undesirable communication may be made between the fracturing fluid or slurry and the surrounding formation. When fracture operations are ceased and a liquid waste slurry such as that as taught by said U.S. Patent No. 3,108,439 is left in the formation, the release of the internal pressure causes the overburden to force the waste slurry into any communicating areas. Such waste material may then find its way into natural fresh water supplies or even to the earth's surface thus polluting clean areas and causing a hazard to anyone coming in contact with the polluted area or polluted fluids therefrom.

The present invention eliminates this dangerous occurrence by adding relatively small amounts of cement, certain clays and other additives to the waste material to cause it to set, after displacement in the underground formation, into a solid mass of sufficient strength that it is substantially unaffected by overburden pressures.

A solid mass having a compressive strength of 50 to 100 p.s.i. is suitable for most disposal operations. Greater or lesser compressive strengths may be had by varying the composition and amounts of additives in the fracturing slurry.

The slurry of the present invention for use in hydraulic fracturing and disposal of waste material in the fractured earth formation, is one which may be pumped for periods of time to allow large quantities to be injected, is economical to prepare, does not exhibit any phase separation, sets into a reasonably hard solid mass, and in the case of radioactive waste materials, adequately retains radioactive nuclides.

It has been discovered that a settable fracturing slurry may be prepared by adding cement, an adsorption type clay like attapulgite, and a chemical cement retarding agent to a waste material for disposal thereof in an underground formation fracture. The slurry must contain sufficient water to form a pumpable slurry. The lower the viscosity of the slurry, the less pumping pressure required to move it. A slurry having a viscosity of about 20 poises or less is preferred and is suitable for most uses.

The liquid waste material most frequently encountered had a viscosity of not more than about 3 poises. The viscosity of high viscosity waste materials can be lowered to the preferred range by the addition of water or other suitable liquids.

Also, in using the above slurry constituents, the waste material must have a pH of 7 or more. The pH of the waste material can be increased by the addition of water thereto or by any other suitable means.

In disposing of radioactive wastes, a material is added to the slurry which has the ability to retain radioactive isotopes by adsorption, ion exchange or some other mechanism.

In disposing of a typical synthetic waste solution containing radioactive isotopes or nuclides, water and chemicals as follows:

Chemical:	Molar concentration
Sodium hydroxide -----	0.220
Sodium nitrate -----	0.315
Sodium sulfate -----	0.037
Sodium chloride -----	0.006
Aluminum nitrate -----	0.022
Ammonium nitrate -----	0.025

a slurry may be prepared by using materials and amounts as follows:

Material:	Amount
Portland cement ---	3-10 lbs./gal. of waste.
Attapulgite clay ---	4-25% by weight of cement.
Illite clay -----	4-15% by weight of cement.
Chemical cement	
retarder -----	0.1-0.5% by weight of cement.

A slurry mix suitable for disposal of most types of liquid radioactive wastes in generally impervious bedded-shale formations is as follows:

Amount	Material	Purpose
>5.0 lbs./gal. ¹ -----	Cement-----	Strength.
8-10 wt. percent ² ---	Attapulgus-150-----	Suppresses phase separation.
6-8 wt. percent ² ---	Grundite clay-----	Cesium retention.
0.2-0.3 wt. percent ² ---	Delta glucosyl lactone-----	Retards setting.
200-400 p.p.m.-----	Tributylphosphate ³ ---	Foam suppressor.

¹ Of liquid waste.

² By weight of cement.

³ Optional.

In waste materials having low ionic content, bentonite or other similar type clays may be substituted for the attapulgite clay, either in whole or in part, depending upon amount of radioactive ions present. Bentonite is a good water retention agent, but flocculates in the process of high ionic content wastes. Attapulgite clay, and par-

ticularly Attapulgius-150, does not flocculate and is very effective in preventing phase separation, thus enabling a constant viscosity and a constant cement/liquid ratio for the desired strength to be maintained. Without the specific material, Attapulgius-150, substantially larger amounts of cement would be required; thus significantly increasing the cost of the mix. However, for wastes of low ionic content it may be desirable to use bentonite in replacement of part of the attapulgius to maintain low viscosity without phase separation.

It was found that radioactive cesium is the nuclide most easily leached from radioactive waste-containing cement. Thus, it is desirable to provide for increased retention of this and other "problem" nuclides. The mineral Illite, the principal constituent of Grundite clay, is effective in retaining cesium; therefore, the Grundite clay was added for this purpose.

Most cement-clay mixes set up rather rapidly, e.g., 2-3 hours. For injection of significant quantities of the waste by the fracturing method, the mix must retain its fluidity for several times that length of time, e.g., 15-20 hours. The salts within the waste may contribute partially to the setting retardation; however, it is necessary to extend the setting time. A relatively small amount of delta glucono lactone extends the setting time to the order of 18-20 hours. Other suitable cement retarding agents may be used, including calcium lignosulfonate and calcium-sodium lignosulfonate.

In practice, a control is needed to regulate the addition of dry constituents to the liquid waste. One effective method is that of measuring the density of the resultant slurry and varying the additions to maintain the desired density. Difficulty may be encountered in this measurement because of foam sometimes produced in the process of mixing the solids and waste liquid. There are antifoaming agents used in other chemical processes, including several organic materials which may be used to control foam. Tributylphosphate was found to be effective when present in less than 300 parts per million concentration in the waste. Any suitable anti-foaming agent may be used.

The clays discussed herein are defined as follows:

Attapulgius.—The chief mineral in the fuller's earth from Florida and Georgia, U.S.A. An extensive replacement of Al for Mg is possible in its formula.

Attapulgius-150.—Trade name of an attapulgius clay manufactured by Minerals and Chemicals Corp. of America.

Bentonite.—A rock composed essentially of mixture of montmorillonite and beidellite with the former predominating—also a trade name given to highly adsorptive clays or "swelling" drilling muds.

Illite Group.—A group related to the micas and of a complex chemical composition with the general formula $(OH)_4K_y(Al_4Fe_4Mg_4Mg_6)(Si_{8-y}Al_y)O_{20}$. This group embraces the most common and widespread of the clay minerals and is the chief constituent of clay minerals and shales.

Illite.—A general term for a group of mica-like minerals so common in argillaceous sediments; not a specific mineral species.

Grundite.—A trade name for a non-bentonitic clay allied to illite and coming from Grundy County, Illinois.

A typical example of the disposal of radioactive waste by hydraulic fracturing is as follows. An injection well is drilled to a depth of 1000 feet into an impermeable bedded-shale formation. This well is cased to the bottom with cement used as a sealant between the casing and the rock. One or more observation wells are placed along what is expected to be the periphery of the grout sheet produced by the fracturing. Casings are similarly sealed in these wells. A sand-jet tool is lowered into the injection well to a depth of about 890 feet (other injections having been made at lower depths) and a sand-water mixture is forced through the jet at high pressure, at the same time the jet is rotated, to achieve the slotting of the casing (and any adjacent cement). For example, 10-20 mesh sand is

used in water with a pressure of 3000 to 3700 p.s.i. and the casing is penetrated in about ½ hour. The initial fracture of the rock may be made at this time, or following the withdrawal of the slotting jet, by hydraulically pressurizing the well at the slot at about 4000 p.s.i. (as measured at the well head). The character of the rock may be determined by a fluid-loss test; that is, measuring the rate and amount of bleedback fluid following separate injections of a given amount of water (e.g., 1700 gal.) at a selected pressure followed by the injection of the same amount of water to which is added a given amount of fluid-loss-additive. If any significant difference is noted, a fluid-loss-additive may be required in the final cement mixture.

After a thorough blending (in batches) of 723,000 pounds of Portland Type II Cement, 72,300 pounds of Attapulgius-150, 50,700 pounds of Grundite and 2,170 pounds of delta glucono lactone, this is thoroughly mixed in proper proportion with 148,000 gallons of a radioactive waste solution as the resultant slurry is pumped into the well at an average rate of 240 gallons per minute at a pressure of 2000 p.s.i. At this pressure the rock fracture is extended until after about 11 hours the entire slurry is pumped into the fracture. Thereafter, a small quantity of normal cement mixture, i.e., the same as the above mixture without containing any radioactive materials, is pumped through the system to flush out remaining radioactivity-containing slurry and to fill the well casing in the vicinity of the injection slot.

This tail-out slurry not only functions as a flush, but also provides a strong plug behind the waste containing slurry. This tail-out or normal cement slurry is preferably a normal ASTM Type I or Type II cement prepared using fresh water and does not contain any waste fluid. It is somewhat faster setting than the waste disposal slurry and sets to a higher compressive strength.

Throughout the pumping, the observation wells are frequently "logged" to determine the pattern of the grout sheet, and the level thereof, as the grout approaches or passes around the observation well. This primarily assures that the grout sheet remains at a level where future release to the environment is improbable. Since these wells are cased, the escape of grout up the well shaft is prohibited.

Subsequently, if desired, additional injections may be made at decreasing depths in the injection well by utilizing the same method.

In an actual fracturing disposal operation, an injection well was drilled to a depth of 1,055 feet and cased with 157 feet of 9½"-36#-J55 surface casing and 1,050.96 feet of 5½"-23#-N80 Extreme Line casing cemented to the surface. The injection tubing was 2½"-6.4#-N80 Extreme Line tubing.

The casing was slotted at 890.00 feet using 40 sacks of 10-30 sand and a pump pressure up to 3,800 p.s.i.

211,275 gallons of fracturing slurry which consisted of 1,216,390 pounds of dry material mixed with 147,600 gallons of liquid waste and approximately 4,200 gallons of water was pumped into the injection well. These quantities exceeded the storage capacity of the plant, and both liquid and dry materials were added to the storage during the actual injection. The total injection time was 11 hours and the job was completed without interruption. The formation was broken down with 1,992 gallons of water at 5,000 p.s.i. pressure. The injection was made starting with an initial pressure of 3,800 p.s.i., which decreased rapidly to an average injection pressure of about 1,900 p.s.i. Throughout the 11 hours of pumping, the injection rate averaged approximately 8 barrels per minute.

The liquid waste material contained 5000 curies of cerium and synthetic waste solution as set forth hereinabove. Cerium was added so that core samples could be taken from the observation well and the grout sheet formed by this slurry could be distinguished from the

grout sheets previously formed. The fracturing slurry was made up as follows:

Synthetic waste solution (containing 5000 curies of cerium).

6.5 pounds Volunteer Type II Cement/gallon of waste solution.

0.65 pound of Attapulgius-150/gallon of waste solution.

0.45 pound Grundite Bond Clay/gallon of waste solution.

0.02 pound delta glucono lactone/gallon of waste solution.

250-500 p.p.m. in waste solution of tributyl phosphate anti-foaming agent.

Table I hereinbelow summarizes the injection operation.

TABLE I

First day

#4 plug at 900 ft. injection over-displaced. Mixed 20 sack cement plug, calculated top 890 ft.

Second day

Cement plug held -----p.s.i. 3000

Actual top of cement plug -----ft. 894.66-900.0

Hydra-Jet at 890 ft., 10:30 to 10:45 A.M.:

40 sacks of 10-30 mesh sand.

Maximum jetting pressure -----p.s.i. 3800

5000 gal. water from waste pit with 400 p.p.m. tributyl phosphate to control foam.

Breakdown pressure -----p.s.i. 5000

Fourth day

Injection at 890 ft., 7:10 A.M. to 6:00 P.M.:

2nd breakdown pressure -----p.s.i. 3900

1,037,000# cement; 103,700# Attapulgi-

150; 72,590# Grundite clay and 3,100#

delta glucono lactone mixed at 12.35#/gal.

147,600 gal. waste at 8.3#/gal.

Average injection pressure -----p.s.i. 1900

Average slurry injection rate -----g.p.m. 330

Total slurry (pump counter) -----gal. 211,275

20-sack cement plug calculated top -----ft. 890

Tubing in hole while injecting -----ft. 838.88

In carrying out the above operation, ASTM Type II cement was used rather than ASTM Type I, as the synthetic waste had a high sulfate content. The Type II cement offered some degree of protection from the deleterious effect of the sulfate. Similar slurry properties were obtained with both types of cements.

A number of tests were made with various concentra-

tions of additives and waste solution. For purposes of this testing program, the chemical content of the waste solution was designated as 1X, with X being a normal waste solution as follows—

Chemical:	Concentration, molar
Sodium hydroxide -----	0.220
Sodium nitrate -----	0.315
Sodium sulfate -----	0.037
Sodium chloride -----	0.006
Aluminum nitrate -----	0.022
Ammonium nitrate -----	0.025

Cement slurries were tested over the range of 0.1X to 10X. Some data were obtained wherein only the sodium hydroxide was varied since this chemical is known to effect the setting of cement. Slurry design was based on a solution containing sodium carbonate in a concentration of 0.02 molar in the 1X waste. The results of these tests are recorded in the tables hereinbelow. All measurements were made in accordance with standard API procedures (API RP 10B). All percentage figures are by weight of cement. Where no data is shown, measurements were not made, but all slurries set into a hard mass within 28 days, and most within 14 days.

TABLE II.—COMPONENTS OF SLURRIES

[Slurry evaluation data, volunteer type II cement, tributyl phosphate at 250 p.p.m. in waste]

	Cement, Sly. No.	lbs./gal.	Waste, strength	Attapulgius 150, percent	Bentonite, percent	Grundite, percent	Retarder, ¹ percent
30	1-----	6.5	0.1X	10.0	3.5	-----	0.3
	2-----	6.5	0.1X	10.0	-----	7.0	0.2
	3-----	6.5	0.1X	10.0	-----	7.0	0.3
	4-----	6.5	0.5X	10.0	3.5	-----	0.2
	5-----	6.5	0.5X	10.0	3.5	-----	0.3
	6-----	6.5	0.5X	10.0	-----	7.0	0.2
	7-----	6.5	0.5X	10.0	-----	7.0	0.3
35	8-----	6.5	1X	10.0	-----	7.0	0.2

¹ Delta glucono lactone.

PROPERTIES OF SLURRIES

	Sly. No.	Viscosity Poises, 20 min.	Water Separation, cc./250 cc.	Thickening Time, 89° F., hrs.:min.	Compressive Strength, 7 days at 80° F.
40	1-----	9	1.4	-----	-----
	2-----	-----	-----	38:00+(36)	40
	3-----	6	1.4	-----	-----
	4-----	7	2.5	-----	-----
	5-----	4	2.3	-----	-----
	6-----	4	0.6	16:58 (70)	230
45	7-----	3	4.2	33:00+(16)	200
	8-----	-----	-----	17:15 (70)	370

¹ Free water reabsorbed when the slurry set.

Figures in parentheses are viscosity at the indicated time.

TABLE III

[Slurry evaluation data, volunteer type II cement, 10 lbs. of cement/gallon of synthetic waste, tributyl phosphate at 250 p.p.m. in waste]

Sly. No.	Attapulgius 150, percent	Bentonite, percent	Retarder, ¹ percent	Viscosity Poises, 20 min.	Water Separation, cc./250 cc.	Thickening Time, 89°, hrs.:min.
1X Synthetic Waste						
1-----	3.8	-----	0.1	2	4.0	10:26(665)
2-----	4.6	-----	0.1	6	0.0	11:51(770)
3-----	5.4	-----	0.1	10	0.0	12:47(465)
4-----	3.8	-----	0.2	1	37.0	-----
5-----	4.6	-----	0.2	2	25.0	-----
6-----	5.4	-----	0.2	3	14.0	-----
7-----	3.8	-----	² 0.5	9	0.7	9:40(845)
8-----	4.2	-----	² 0.5	9	1.0	-----
9-----	4.1	1.5	0.1	7	³ 1.2	11:11(685)
10-----	4.1	1.5	0.15	3	-----	20:00(980)
11-----	4.1	1.5	0.2	2	0.0	26:10(1060)
12-----	3.6	2.0	0.1	3	4.6	-----
13-----	3.6	2.0	0.2	1	22.7	-----
14-----	2.6	4.0	0.1	2	17.8	-----
0.1X Synthetic Waste						
15-----	3.8	-----	0.1	3	5.0	-----
16-----	4.6	-----	0.1	5	5.4	12:55(495)
17-----	5.4	-----	0.1	8	3.0	11:52(595)
18-----	3.8	-----	0.2	3	13.0	-----
19-----	4.6	-----	0.2	4	7.0	-----
20-----	5.4	-----	0.2	6	5.0	-----
21-----	3.8	-----	² 0.5	3	11.6	-----
22-----	4.2	-----	² 0.5	4	10.0	-----
23-----	4.1	1.5	0.1	8	³ 2.0	12:25(715)
24-----	4.1	1.5	0.15	8	³ 2.0	-----
25-----	4.1	1.5	0.2	7	1.9	-----

¹ Delta glucono lactone.

² Calcium lignosulfonate in lieu of delta glucono lactone.

³ Free water reabsorbed when the slurry set.

Figures in parentheses—compressive strength at 80° F. and 7 days after pumping for indicated time.

TABLE IV

[Slurry evaluation data, 10X synthetic waste solution, volunteer type I and type II cements]

Sly. No.	Attapulugus 150, lb./ gal., 10X waste	Retarder, percent	Viscosity Poises, 20 min.	Water Separation, cc./250 cc.	Fluid Loss., cc./30 min.		Thickening, Time, to 30 poises, ¹ 1,000 ft., 89° F., hrs.:min
					100 p.s.i.	1,000 p.s.i.	
4Lbs. Type I Cement/Gallon of 10X Waste							
1-----	0.278	² 1.5	2	0.8	138	278	6:26
2 ³ -----	0.500	⁴ 0.3	5	1.0	163	302	-----
3 ⁴ -----	0.600	⁴ 0.3	8	0.8	145	256	-----
4 ⁵ -----	0.700	⁴ 0.3	9	0.1	131	226	8:22
5 ⁶ -----	0.700	⁴ 0.4	-----	-----	-----	-----	11:17
6 ⁷ -----	0.700	² 2.0	-----	-----	-----	-----	5:07
7 ⁸ -----	0.700	² 2.5	-----	-----	-----	-----	6:08
5 Lbs. Type I Cement/Gallon of 10X Waste							
8-----	0.278	² 1.5	3	0	172	258	-----
9-----	0.347	² 1.5	4	0	134	226	3:49
10 ¹ -----	0.347	² 1.5	1	0.4	164	278	4:09
11 ² -----	0.347	² 2.0	-----	-----	-----	-----	4:49
12 ³ -----	0.347	² 2.5	-----	-----	-----	-----	5:48
13-----	0.347	⁴ 0.2	1	1.7	208	406	5:57
14 ⁴ -----	0.347	⁴ 0.2	-----	1.5	-----	-----	6:11
15 ⁵ -----	0.347	⁴ 0.3	2	0.9	211	392	10:14
16 ⁶ -----	0.500	⁴ 0.3	5	1.0	(160)	(292)	9:30
17 ⁷ -----	0.600	⁴ 0.3	9	0.7	139	254	-----
18 ⁸ -----	0.700	⁴ 0.3	12	0.2	124	218	-----
5 Lbs. Type II Cement/Gallon of 10X Waste							
19 ¹ -----	0.500	⁴ 0.2	8	0	146	294	7:18
20 ² -----	0.500	⁴ 0.3	3	0.8	158	302	11:20
6 Lbs. Type II Cement/Gallon of 10X Waste							
21-----	0.278	⁵ 1.5	3	0	146	312	-----

[Compressive Strength, p.s.i. at 650° F. and indicated curing time]

Sly. No.	2 Days	3 Days	4 Days	7 Days	10 Days	14 Days	28 Days
2 ³	90	135	-----	260	-----	345	175
9.....	45	85	-----	125	-----	-----	70
14 ⁴	130	200	-----	360	-----	365	190
15 ⁵	95	180	-----	320	-----	355	210
16 ⁶	130	220	-----	360	-----	370	325
19 ⁷	85	-----	175	-----	275	-----	-----
20 ⁸	35	-----	170	-----	250	-----	-----

¹ Thickening times are to 30 poises viscosity because low quantities of cement do not permit attainment of 70 poises.² Calcium lignosulfonate.³ Slurries contained tributyl phosphate de-foamer at a ratio of 1 quart/1000 gallons of 10X waste.⁴ Delta glucono lactone.

TABLE V

[Slurry evaluation data, 10X synthetic waste solution, volunteer type I cement]

Sly. No. ¹	Cement, lb./gal., 10X waste	Retarder, Percent ²	Viscosity Poises, 20 min.	Water Separation, cc./250 cc.	Fluid Loss, cc./30 min.		Thickening Time to 30 poises, 1,000 ft., 89° F., hr.:min.
					100 p.s.i.	1,000 p.s.i.	
0.5 Lb. Attapulgu 150/Gallon of 10X Waste							
21-----	5.25	0.3	5	1.3	166	308	9:07
22-----	5.5	0.3	5	1.0	164	316	8:58
23-----	5.75	0.3	7	0.7	154	300	9:17
24-----	6.0	0.3	6	1.2	156	308	9:07
25-----	5.5	0.27	6	1.6	156	300	8:14
26-----	6.0	0.25	6	0.7	151	294	7:37
0.7 Lb. Attapulgu 150/Gallon of 10X Waste							
27-----	2.0	0.3	4	0.4	139	220	-----
28-----	2.0	0.75	2	Trace	134	212	-----
29-----	3.0	0.3	8	0.2	137	232	-----
30-----	3.0	0.5	7	Trace	136	226	-----

¹ Slurries contained tributyl phosphate de-foamer.² Delta glucono lactone.

TABLE VI

Compressive strength—pumped slurries

Two inch cube specimens were prepared from slurries used for thickening measurement, after attainment of the terminal viscosity of 30 poises. These cubes were cured for 7 days, less the thickening time, at 80° F. prior to crushing for strength.

Slurry No., Tables IV and V:	Compressive strength, p.s.i.
16 ¹	105
19 ¹	140
20 ¹	90
21 ¹	125
22 ¹	170
23 ¹	165
24 ¹	180
25 ¹	140
26 ¹	200

¹ Slurries contained tributyl phosphate de-foamer.

It can be appreciated that the present invention while 75

being particularly suitable for the disposal of waste materials containing radioactive nuclides or isotopes, it is also suitable for disposal of any other waste materials, such as non-radioactive industrial wastes and sewage products.

In disposing of non-radioactive wastes, while it is desirable that the water phase separation be low, it is not necessary that it be as low as in the case of disposing of radioactive wastes. The small amount of liquids (non-radioactive) which might ultimately escape to the earth's surface could be sufficiently filtered so as not to pollute or contaminate surrounding areas. However, though, to prevent pollution of underground fresh water streams, the water phase separation should be relatively low.

A water phase separation in the slurry of less than about 1% is preferred, especially when disposing of radioactive wastes. However, greater water phase separation may be permitted, as some water adsorption is made by the formation adjacent the slurry. The amount of the adsorption will of course vary somewhat with the type of formation being fractured.

Although the present invention is especially adapted

for disposal of waste materials in substantially impermeable or bedded-shale formations, the invention is not so limited and may be carried out in any type of earth formation found to be satisfactory.

Although no field work has been done, the present invention may be effective for disposal of waste materials in even incompetent sands, wherein actual fracturing is not necessary, but just a mere injection of the slurry into the formation and subsequent setting thereof.

Broadly, the present invention relates to a new and improved method of disposing of wastes in an underground earth formation, wherein such wastes are introduced into the formation in a highly liquid or low viscosity state and then allowed to set into a hard mass, with the mass being substantially confined to the area injected therein.

The foregoing disclosure and description of the invention is illustrative and explanatory thereof and various changes in the size, shape and materials, as well as in the details of the illustrated method and composition, may be made within the scope of the appended claims without departing from the spirit of the invention.

What is claimed is:

1. A method of subterranean disposal of radioactive materials, which comprises: providing a wellbore having a casing therein which penetrates an earth formation; fracturing through said earth formation to provide at least one fracture which extends into the formation at an angle with respect to the axis of said wellbore; injecting into a fracture so formed in the earth formation a settable fracturing slurry having a viscosity of less than about 20 poises, consisting essentially of the radioactive waste material, water in a sufficient amount to provide the required slurry viscosity, hydraulic cement in an amount of from about 3 to about 10 pounds per gallon of waste and water, an attapulgite clay in an amount of about 25% to about 4% by weight of cement, an illite type clay in an amount of about 15% to about 4% by weight of cement and a chemical retarding agent in amount sufficient to delay the setting of the slurry a relatively long period of time and subsequently permit the slurry to set into a hard mass; and, allowing the slurry to set in the formation fracture into a hard mass, thereby substantially confining the waste material in the formation fracture.

2. The method of claim 1, wherein the slurry contains a sufficient amount of an anti-foaming agent to substantially inhibit the formation of any foam in the slurry.

3. The method of claim 2, wherein the anti-foaming agent is tributyl phosphate.

4. The method of claim 1, wherein the hydraulic cement is selected from the group consisting of ASTM Type I cement and ASTM Type II cement.

5. The method of claim 1, wherein the chemical retarding agent is delta glucono lactone in an amount of about 0.1% to about 0.5% by weight of cement.

6. The method of claim 1, wherein the chemical retarding agent is a lignosulfonate.

7. The method of claim 1, wherein a clay selected from the group consisting of a bentonite type clay and mixtures of a bentonite type clay and an attapulgite type clay is substituted for the attapulgite clay.

8. A method of subterranean disposal of radioactive material, which comprises: providing a wellbore having a casing therein which penetrates an earth formation; fracturing through said earth formation to provide at least one fracture which extends into the formation at an angle with respect to the axis of said wellbore; injecting into a fracture so formed in the earth formation a settable fracturing slurry having a viscosity of less than about 20 poises, less than about one percent water separation, a thickening time of from about 15 to about 18 hours and upon setting has a compressive strength of at least about 50 pounds per square inch; said slurry consisting essentially of the radioactive waste material, water in a sufficient amount to provide the required slurry viscosity, hydraulic cement in an amount sufficient to provide the required compressive strength, an attapulgite clay in an amount sufficient to provide the required minimum water separation, an illite type clay in an amount sufficient to substantially absorb the radioactive ions present in the slurry, and a cement retarding agent in an amount sufficient to provide the required delay in thickening of the slurry; and, allowing the slurry to set into a hard mass, thereby substantially confining the waste material in the formation fracture.

9. The method of claim 8, wherein said cement is selected from the group consisting of ASTM Type I cement and ASTM Type II cement and is present in an amount less than about 6 pounds per gallon of waste material and water, said attapulgite type clay is present in an amount of from about 8 to about 10% by weight of cement, said illite type clay is present in an amount of from about 6 to about 8% by weight of cement, and said retarding agent is delta glucono lactone in an amount of from about 0.2% to about 0.3% by weight of cement.

10. The method of claim 9, wherein the slurry contains from about 200 to about 400 parts per million of tributyl phosphate anti-foaming agent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,379,013

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Knox A. Slagle et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 64, after "is" insert -- ceased, and the fracture is --. Column 2, line 62, after "become" insert -- more --. Column 8, TABLE II, lower portion, heading to the last column, line 2 thereof, after "Strength," insert -- p.s.i., --. Columns 9 and 10, TABLE IV, about the middle of the table, in the heading, "650° F." should read -- 65° F. --.

Signed and sealed this 17th day of March 1970.

(SEAL)

Attest:

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